J. Phys. Chem. A **2004,** *108,* 5635−5642

Atmospheric Chemistry of 4:2 Fluorotelomer Alcohol ($CF_3(CF_2)_3CH_2CH_2OH$): Products and Mechanism of Cl Atom Initiated Oxidation

M. D. Hurley,* J. C. Ball, and T. J. Wallington

Ford Motor Company, SRL-3083, PO Box 2053, Dearborn, Michigan 48121-2053

M. P. Sulbaek Andersen

Department of Chemistry, University of Copenhagen, Universitetsparken 5, DK-2100 Copenhagen, Denmark

D. A. Ellis, J. W. Martin, and S. A. Mabury

Department of Chemistry, 80 St. George St., University of Toronto, Toronto, Ontario, Canada M5S 3H6

Received: February 12, 2004; In Final Form: April 2, 2004

Smog chamber/FTIR techniques were used to study the products and mechanism of the Cl atom initiated oxidation of 4:2 fluorotelomer alcohol ($CF_3(CF_2)_3CH_2CH_2OH$) in 700 Torr of N_2/O_2 diluent at 296 K. $CF_3(CF_2)_3CH_2CHO$ is the sole primary oxidation product. $CF_3(CF_2)_3CHO$, $CF_3(CF_2)_3CH_2COOH$, and $CF_3(CF_2)_3CH_2C(O)OOH$ are secondary oxidation products. Further irradiation results in the formation of $CF_3(CF_2)_3COOH$, COF_2, and CF_3OH. $CF_3(CF_2)_3CHO$, $CF_3(CF_2)_3CH_2COOH$, and $CF_3(CF_2)_3CH_2C(O)OOH$ are formed from $CF_3(CF_2)_3CH_2CHO$ oxidation in yields of 46%, 27%, and ≤27%, respectively. Using relative rate techniques, a value of $k(Cl + CF_3(CF_2)_3CH_2CHO) = (1.84 \pm 0.30) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} was determined. The yield of the perfluorinated acid, $CF_3(CF_2)_3COOH$, from the 4:2 fluorotelomer alcohol increased with the diluent gas oxygen concentration. For the experimental conditions used herein and employing >98% consumption of 4:2 fluorotelomer alcohol, the molar yields of $CF_3(CF_2)_3COOH$ were <0.011, 0.031, 0.042, and 0.056 in experiments conducted with 10, 140, 400, and 700 Torr O_2, respectively. These results suggest that the atmospheric oxidation of fluorotelomer alcohols may be a significant source of the perfluorinated carboxylic acids that are observed in remote areas.

1. Introduction

Fluorotelomer alcohols (FTOH) are linear, fluorinated alcohols with the formula $CF_3(CF_2)_nCH_2CH_2OH$ ($n = 1, 3, 5, ...$) and are used in a variety of industrial products, such as paints, coatings, polymers, adhesives, waxes, polishes, electronic materials, and caulks. The telomerization process results in even-numbered chain lengths and the alcohols are named according to the number of fluorinated and hydrogenated carbons. The fluorotelomer alcohol considered in this study, $CF_3(CF_2)_3CH_2CH_2OH$, is referred to as 4:2 fluorotelomer alcohol or 4:2 FTOH. Global production of fluorotelomer alcohols is estimated to be 5×10^6 kg year^{-1} with 40% produced in North America.[1] Fluorotelomer alcohols are volatile, appear to be ubiquitous in the North American atmosphere (17−135 pg m^{-3}),[2,3] have an atmospheric lifetime (11−20 days) sufficient for widespread hemispheric distribution,[4,5] and have a long perfluoroalkyl moiety. These properties make fluorotelomer alcohols plausible candidates as precursors of perfluorinated carboxylic acids observed in the environment.

Perfluorinated carboxylic acids (PFCA) have the formula $CF_3(CF_2)_nCOOH$ and are highly persistent in the environment. PFCAs resist degradation via oxidation, hydrolysis, or reduction under biotic and abiotic conditions.[6] Analysis of rainwater indicates the widespread occurrence of short-chain PFCAs ($n = 2-7$) at low levels (~1−100 ng/L).[7] Perfluorinated acids are bioaccumulative when the perfluorinated chain is more than six carbons in length. Long-chain PFCAs, $n = 5-11$, have been observed in fish from the Great Lakes[8] and in arctic fish and mammals.[9] Perfluorooctanoic acid (PFOA) is potentially toxic[10−12] and the health effects associated with long-term exposure are the subject of a current risk assessment.[13]

Other than for trifluoroacetic acid (TFA),[14] no natural source of PFCAs has been proposed. PFCAs with a chain length of $n = 1-12$ are minor products emitted to the atmosphere from thermolysis of fluoropolymers;[15] however, the thermolysis of fluoropolymers is unlikely to make a significant contribution to the observed global burden of PFCAs. Water-soluble PFCA salts are used in the processing of fluoropolymers and may enter local aquatic environments directly; however, it is difficult to explain how involatile PFCA salts would be transported to remote regions since they are removed from the atmosphere via wet and dry deposition on a time scale of a few days.[16] The simplest explanation for their ubiquity in biota in remote regions is that there are anthropogenic precursors in the atmosphere that degrade to PFCAs.

In a recent study by Ellis et al.,[17] the Cl initiated oxidation of 4:2 FTOH, 6:2 FTOH, and 8:2 FTOH resulted in the formation of $CF_3(CF_2)_nCOOH$, $n = 0-7$. A detailed understanding of the atmospheric oxidation mechanism of fluorotelomer alcohols is needed to assess the contribution, if any, of their atmospheric oxidation to global PFCA pollution. Unfortunately, there are few available data concerning the atmospheric chemistry of fluorotelomer alcohols and assessments of their environmental fate are uncertain. To improve this situation,

---

* Corresponding author. E-mail: mhurley3@ford.com.

10.1021/jp0493576 CCC: $27.50

we have conducted an experimental study of the Cl atom initiated oxidation of $CF_3(CF_2)_3CH_2CH_2OH$ (4:2 FTOH) in 700 Torr of N_2/O_2 diluent at 296 K in the absence of NO_x. Results are discussed with respect to the atmospheric oxidation of fluorotelomer alcohols.

2. Experimental Section

Experiments were performed in a 140-L Pyrex reactor interfaced to a Mattson Sirus 100 FTIR spectrometer.[18] The reactor was surrounded by 22 fluorescent blacklamps (GE F15T8-BL) which were used to photochemically initiate the experiments. Chlorine atoms were produced by photolysis of molecular chlorine.

$$Cl_2 + h\nu \rightarrow Cl + Cl \qquad (1)$$

The loss of $CF_3(CF_2)_3CH_2CH_2OH$ was monitored by FTIR spectroscopy using an infrared path length of 27 m and a resolution of 0.25 cm^{-1}. Infrared spectra were derived from 32 co-added interferograms. Liquid reagents or reference compounds were introduced into the chamber by transferring the vapor above the liquid via a calibrated volume. Similarly, gaseous reagents were introduced into the chamber via a calibrated volume. The contents of the calibrated volume were swept into the chamber with the diluent gas (air, oxygen, or nitrogen).

Reactant and reference compounds were monitored using absorption features at the following wavenumbers (cm^{-1}): $CF_3(CF_2)_3CH_2CH_2OH$, 3672; $CF_3(CF_2)_3CH_2CHO$, 1752; $CF_3(CF_2)_3CH_2COOH$, 1794; $CF_3(CF_2)_3CHO$, 1778; and COF_2, 1944. Initial reagent concentrations for Cl atom initiated oxidation experiments were 6.1−34.4 mTorr of $CF_3(CF_2)_3CH_2CH_2OH$ and 77−100 mTorr of Cl_2 in 700 Torr of diluent (air, oxygen, or nitrogen). All experiments were performed at 296 K. Reagent and reference compounds were obtained from commercial sources when possible.

$CF_3(CF_2)_3CH_2CHO$, $CF_3(CF_2)_3CHO$, and $CF_3(CF_2)_3CH_2COOH$ were synthesized using procedures described in the literature[19,20] and authenticated by use of IR, NMR, and mass spectrometry. Difficulties handling the small quantities of $CF_3(CF_2)_3CH_2CHO$ prepared by our synthesis were compounded by the low vapor pressure of this material and precluded an absolute calibration of its spectrum (see further discussion in section 3.2). The peracid, $CF_3C(O)OOH$, was prepared by reacting trifluoroacetic anhydride with concentrated H_2O_2. Concentrated hydrogen peroxide was prepared from 50% commercial grade hydrogen peroxide by removing water-enriched vapor under vacuum. An equal volume of dichloromethane was added to the concentrated hydrogen peroxide (assumed to be 90%) followed by a stoichiometric amount of trifluoroacetic anhydride, assuming a molar ratio of 1:1 for the reaction of hydrogen peroxide and the trifluoroacetic anhydride. Dichloromethane and any unreacted trifluoroacetic anhydride were removed under a stream of dry nitrogen gas. We caution against using an excess of the trifluoroacetic anhydride because of the possible formation of the potentially explosive trifluoroacetyl peroxide.[21] All reagents and reference compounds were subjected to repeated freeze−pump−thaw cycling before use.

In smog chamber experiments, it is important to check for unwanted loss of reactants and products via photolysis, dark chemistry, and heterogeneous reactions. Control experiments were performed in which mixtures of reactants (except Cl_2) were subjected to UV irradiation for 15−30 min and product mixtures obtained after the UV irradiation of reactant mixtures were allowed to stand in the dark in the chamber for 15 min. There was no observable loss of reactants or products, suggesting that photolysis, dark chemistry, and heterogeneous reactions are not a significant complication in the present work. Unless stated otherwise, quoted uncertainties are two standard deviations from least-squares regressions.

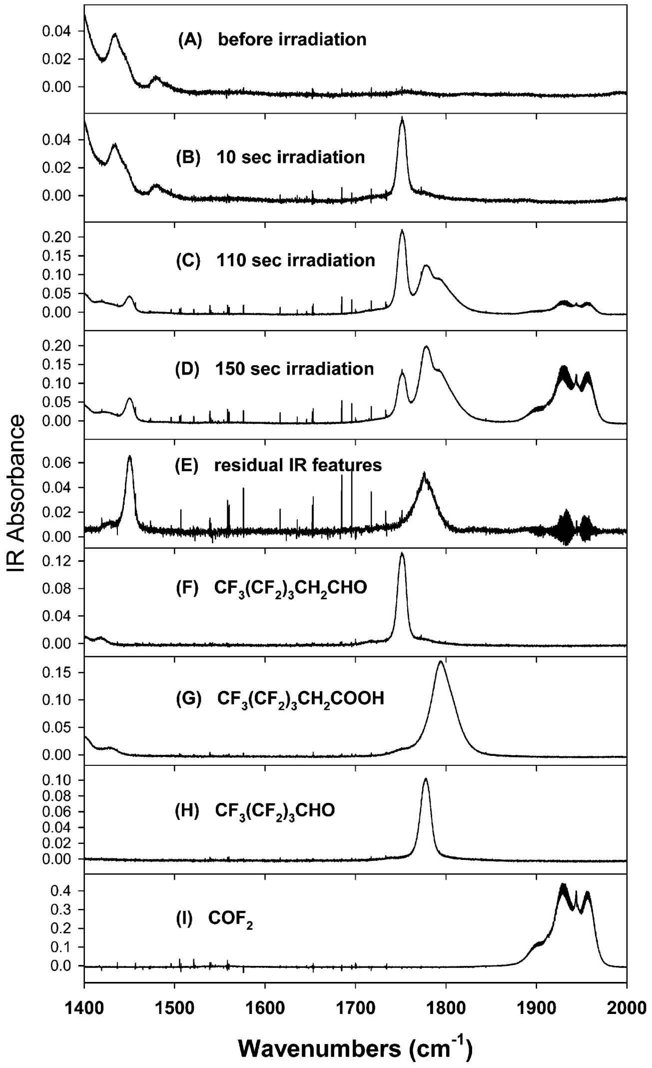

Figure 1. IR spectra obtained before (A) and after 10 s (B), 110 sec (C), and 150 s (D) of irradiation of a mixture of 13.2 mTorr $CF_3(CF_2)_3CH_2CH_2OH$ and 81 mTorr Cl_2 in 700 Torr air. Panel E shows residual IR features present after subtraction of reactant and product reference spectra from the spectrum shown in D. Panels F, G, H, and I are reference spectra $CF_3(CF_2)_3CH_2CHO$, $CF_3(CF_2)_3CH_2COOH$, $CF_3(CF_2)_3CHO$, and COF_2, respectively.

3. Results

3.1. Loss of $CF_3(CF_2)_3CH_2CH_2OH$. The mechanism of Cl atom initiated oxidation of $CF_3(CF_2)_3CH_2CH_2OH$ was investigated by irradiating mixtures of $CF_3(CF_2)_3CH_2CH_2OH$ and Cl_2 in 10, 140, 400, and 700 Torr oxygen. In all experiments, nitrogen was added to provide 700 Torr total pressure. Figure 1 shows spectra acquired before (A) and after 10 (B), 110 (C), and 150 s (D) irradiation of a mixture of 13.2 mTorr $CF_3(CF_2)_3CH_2CH_2OH$ and 81.0 mTorr Cl_2 in 700 Torr air. The consumption of $CF_3(CF_2)_3CH_2CH_2OH$ in this experiment was 9% (B), 76% (C), and 95% (D). Comparison of the IR features in B, C, and D with reference spectra for $CF_3(CF_2)_3CH_2CHO$ (F), $CF_3(CF_2)_3CH_2COOH$ (G), $CF_3(CF_2)_3CHO$ (H), and COF_2 (I) shows the formation of these compounds. O_3, $CF_3(CF_2)_3COOH$,

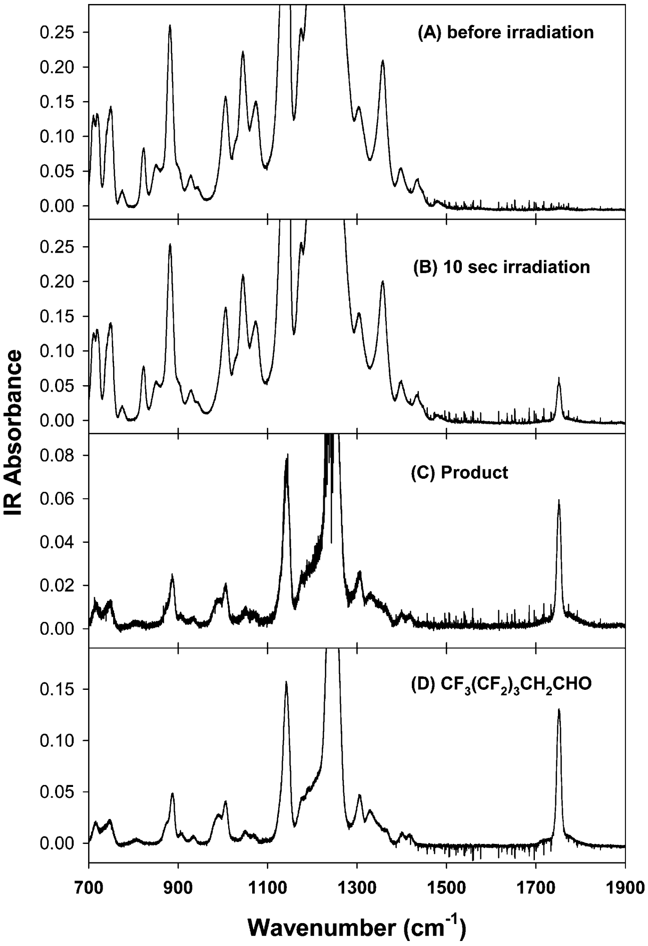

Figure 2. IR spectra obtained before (A) and after (B), 10 s of irradiation of a mixture of 13.2 mTorr $CF_3(CF_2)_3CH_2CH_2OH$ and 81 mTorr Cl_2 in 700 Torr air. Panel C shows the product spectrum obtained by subtracting the IR features of the reactant from the spectrum shown in B. Panel D is the reference spectra of $CF_3(CF_2)_3CH_2CHO$.

and CF_3OH were also observed as products. Figure E shows the residual spectrum after features attributable to $CF_3(CF_2)_3CH_2CH_2OH$, $CF_3(CF_2)_3CH_2CHO$, $CF_3(CF_2)_3CH_2COOH$, $CF_3(CF_2)_3CHO$, and COF_2 were subtracted from Figure D. The features in Figure E are due to an unidentified product which, as discussed in section 3.5, we believe to be the peracid $CF_3(CF_2)_3CH_2C(O)OOH$.

3.2. Formation of $CF_3(CF_2)_3CH_2CHO$ as Primary Product. Figure 2 shows spectra from Figure 1A and B over a wider spectral range. The spectra were acquired before (A) and after (B) a 10-s irradiation of a gas mixture consisting of 13.2 mTorr $CF_3(CF_2)_3CH_2CH_2OH$ and 81.0 mTorr Cl_2 in 700 Torr air. During the irradiation, 9% of the $CF_3(CF_2)_3CH_2CH_2OH$ was consumed. The product spectrum C was obtained by subtracting IR features of $CF_3(CF_2)_3CH_2CH_2OH$ from the spectrum in B. Comparison of the product spectrum C with the reference spectrum in D indicates that $CF_3(CF_2)_3CH_2CHO$ is a major product in the system. After subtraction of features attributable to $CF_3(CF_2)_3CH_2CHO$, there were no residual features that could be attributed to carbon-containing products. In all experiments, employing low consumptions (<10%) of 4:2 FTOH, $CF_3(CF_2)_3CH_2CHO$ was the only observed product. We conclude that $CF_3(CF_2)_3CH_2CHO$ is the sole primary oxidation product of $CF_3(CF_2)_3CH_2CH_2OH$.

This conclusion is consistent with recent work by Hurley et al.[22] in which the chlorine initiated oxidation of $CF_3(CF_2)_nCH_2OH$ ($n = 0-3$) resulted in one primary product: $CF_3(CF_2)_nCHO$ ($n = 0-3$). The reaction of Cl atoms with fluorotelomer alcohols is believed to proceed predominantly (>90%) via attack at the CH_2 group α to the alcohol functionality to give an α-hydroxy alkyl radical.[4] The selectivity of Cl atom attack can be ascribed to a combination of the deactivating effect of fluorine substituents and the activating effect of the alcohol subsituents on the CH_2 groups in the molecule.[4,22] The atmospheric fate of α-hydroxy alkyl radicals is believed to be reaction with O_2 to give the corresponding aldehydes. The initial steps in the chlorine initiated oxidation of $CF_3(CF_2)_3CH_2CH_2OH$ are then

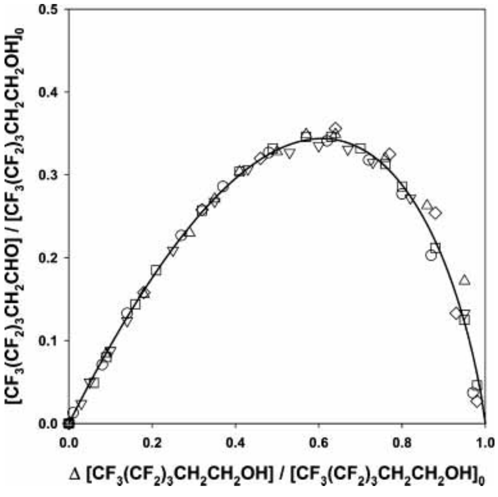

Figure 3. Formation of $CF_3(CF_2)_3CH_2CHO$ versus loss of $CF_3(CF_2)_3CH_2CH_2OH$, normalized for the initial alcohol concentration. Experiments were performed in 700 Torr of N_2/O_2 diluent. Partial pressures of O_2 were 10 Torr, circles; 140 Torr, triangles up and down; 400 Torr, squares; and 700 Torr, diamonds. The line through the data is a fit of eq I to the data.

$$CF_3(CF_2)_3CH_2CH_2OH + Cl \rightarrow CF_3(CF_2)_3CH_2C{\bullet}HOH + HCl \quad (2)$$

$$CF_3(CF_2)_3CH_2C{\bullet}HOH + O_2 \rightarrow CF_3(CF_2)_3CH_2CHO + HO_2 \quad (3)$$

$$CF_3(CF_2)_3CH_2CHO + Cl \rightarrow \text{products} \quad (4)$$

The concentration profile of the reactive primary product, $CF_3(CF_2)_3CH_2CHO$, can be described[23] by the expression

$$\frac{[CF_3(CF_2)_3CH_2CHO]}{[CF_3(CF_2)_3CH_2CH_2OH]_o} = \frac{\alpha(1-x)\{(1-x)^{(k4/k2)-1} - 1\}}{\{1 - (k_4/k_2)\}} \quad (I)$$

where $x = 1 - ([CF_3(CF_2)_3CH_2CH_2OH]/[CF_3(CF_2)_3CH_2CH_2OH]_o)$ is the fractional consumption of $CF_3(CF_2)_3CH_2CH_2OH$, and α is the yield of $CF_3(CF_2)_3CH_2CHO$ from reaction of Cl atoms with $CF_3(CF_2)_3CH_2CH_2OH$ in the presence of oxygen. Figure 3 shows a plot of $[CF_3(CF_2)_3CH_2CHO]/[CF_3(CF_2)_3CH_2CH_2OH]_o$ versus $\Delta[CF_3(CF_2)_3CH_2CH_2OH]/[CF_3(CF_2)_3CH_2CH_2OH]_o$ for five experiments in which the oxygen concentration was varied from 10 Torr to 700 Torr. Because of sample handling problems (see section 2), we were unable to provide an absolute calibration for the reference spectrum of $CF_3(CF_2)_3CH_2CHO$ shown in Figure 1D. Since no other products were observed during the initial irradiations, the reference spectrum of $CF_3(CF_2)_3CH_2CHO$ was calibrated by choosing a calibration for the reference spectrum that results in $\alpha = 1.0$ when eq I is fit to the combined data. Adopting a value of 2.7 mTorr for the $CF_3(CF_2)_3CH_2CHO$ concentration in Figure 2D gives $\alpha = 1.00 \pm 0.03$ and $k_4/k_2 = 1.14 \pm 0.05$. Combining $k_4/k_2 = 1.14 \pm 0.05$ with $k_2 = (1.61 \pm 0.49) \times 10^{-11}$ [4] gives $k_4 = (1.84 \pm 0.30) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}.

3.3. Formation of $CF_3(CF_2)_3CHO$ as a Secondary Oxidation Product. As discussed above, $CF_3(CF_2)_3CH_2CHO$ was the sole primary product of the $CF_3(CF_2)_3CH_2CH_2OH$ oxidation observed in the present experiments. Comparison of Figure 1C and D with the reference spectrum of $CF_3(CF_2)_3CHO$ in Figure 1H shows that $CF_3(CF_2)_3CHO$ is a secondary oxidation product in the system.

The observation of $CF_3(CF_2)_3CHO$ as a secondary product of the Cl initiated oxidation of $CF_3(CF_2)_3CH_2CH_2OH$ is consistent with reactions 2 and 3, followed by abstraction of the aldehydic hydrogen from $CF_3(CF_2)_3CH_2CHO$ and reaction with oxygen to form the acyl peroxy radical, $CF_3(CF_2)_3CH_2C(O)OO\bullet$.

$$CF_3(CF_2)_3CH_2CHO + Cl \rightarrow CF_3(CF_2)_3CH_2C\bullet(O) + HCl \quad (5)$$

$$CF_3(CF_2)_3CH_2C\bullet(O) + O_2 \rightarrow CF_3(CF_2)_3CH_2C(O)OO\bullet \quad (6)$$

The acyl peroxy radical, $CF_3(CF_2)_3CH_2C(O)OO\bullet$, can react with other peroxy radicals to form the alkoxy radical, $CF_3(CF_2)_3CH_2C(O)O\bullet$.

$$CF_3(CF_2)_3CH_2C(O)OO\bullet + ROO\bullet \rightarrow CF_3(CF_2)_3CH_2C(O)O\bullet + RO\bullet + O_2 \quad (7)$$

The alkoxy radical then eliminates CO_2 to form the alkyl radical, $CF_3(CF_2)_3C\bullet H_2$, which will add O_2 and react with other peroxy radicals to give the alkoxy radical, $CF_3(CF_2)_3CH_2O\bullet$.

$$CF_3(CF_2)_3CH_2C(O)O\bullet \rightarrow CF_3(CF_2)_3C\bullet H_2 + CO_2 \quad (8)$$

$$CF_3(CF_2)_3C\bullet H_2 + O_2 \rightarrow CF_3(CF_2)_3CH_2OO\bullet \quad (9)$$

$$CF_3(CF_2)_3CH_2OO\bullet + ROO\bullet \rightarrow CF_3(CF_2)_3CH_2O\bullet + RO\bullet + O_2 \quad (10)$$

Finally, the alkoxy radical, $CF_3(CF_2)_3CH_2O\bullet$, reacts with oxygen to give the observed product, $CF_3(CF_2)_3CHO$.

$$CF_3(CF_2)_3CH_2O\bullet + O_2 \rightarrow CF_3(CF_2)_3CHO + HO_2 \quad (11)$$

On the basis of the mechanism above and assuming no loss of $CF_3(CF_2)_3CHO$ in the chamber, we expect that $CF_3(CF_2)_3CHO$ will increase linearly with $CF_3(CF_2)_3CH_2CHO$ consumption. $CF_3(CF_2)_3CH_2CHO$ is formed in 100% yield from the oxidation of 4:2 FTOH, and $CF_3(CF_2)_3CH_2CHO$ consumption can be equated to the difference between the loss of the parent alcohol and the observed concentration of $CF_3(CF_2)_3CH_2CHO$.

$$\Delta[CF_3(CF_2)_3CH_2CHO] = \Delta[CF_3(CF_2)_3CH_2CH_2OH] - [CF_3(CF_2)_3CH_2CHO] \quad (II)$$

Figure 4 shows a plot of the formation of $CF_3(CF_2)_3CHO$ versus the loss of $CF_3(CF_2)_3CH_2CHO$ calculated from expression II. The formation of $CF_3(CF_2)_3CHO$ and loss of $CF_3(CF_2)_3CH_2CHO$ have been normalized to the initial 4:2 FTOH concentration. The initial slope of the plot in Figure 4 provides information concerning the yield of $CF_3(CF_2)_3CHO$ from oxidation of $CF_3(CF_2)_3CH_2CHO$ while the degree of curvature of the plot provides information concerning the relative reactivity of $CF_3(CF_2)_3CHO$ and $CF_3(CF_2)_3CH_2CHO$ toward Cl atoms.

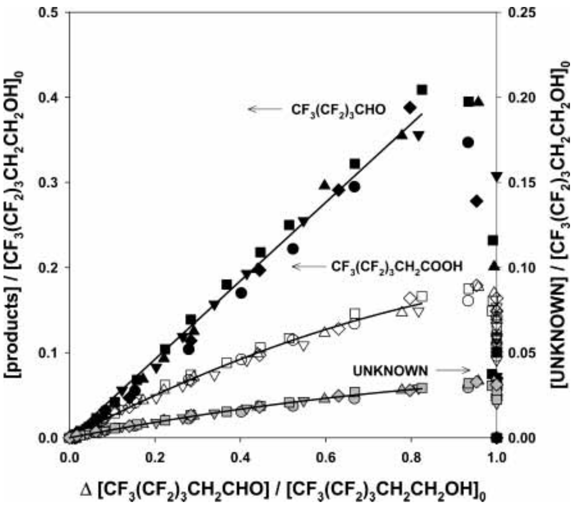

Figure 4. Formation of $CF_3(CF_2)_3CHO$ (black symbols), $CF_3(CF_2)_3CH_2COOH$ (open symbols), and the unknown compounds (grey symbols) versus the loss of $CF_3(CF_2)_3CH_2CHO$, normalized to the initial alcohol concentration. Experiments were performed in 700 Torr of N_2/O_2 diluent. Partial pressures of O_2 were 10 Torr, circles; 140 Torr, triangles up and down; 400 Torr, squares; and 700 Torr, diamonds. The concentration of the unknown is in arbitrary units.

The line through the $CF_3(CF_2)_3CHO$ data in Figure 4 is a linear least-squares fit to the data with $\Delta[CF_3(CF_2)_3CH_2CHO]/[CF_3(CF_2)_3CH_2CH_2OH] < 0.8$ and gives a $CF_3(CF_2)_3CHO$ yield of 0.46 ± 0.03. Curvature is only observed for high consumptions indicating that $CF_3(CF_2)_3CHO$ is significantly less reactive than $CF_3(CF_2)_3CH_2CHO$. This observation is consistent with the fact that Cl atoms are $1.84 \times 10^{-11}/2.1 \times 10^{-12}$ [24] $= 9$ times less reactive toward $CF_3(CF_2)_3CHO$ than toward $CF_3(CF_2)_3CH_2CHO$.

3.4. Formation of $CF_3(CF_2)_3CH_2COOH$ as a Secondary Oxidation Product. Comparison of Figure 1C and D with the reference spectrum of $CF_3(CF_2)_3CH_2COOH$ in Figure 1G shows the formation of $CF_3(CF_2)_3CH_2COOH$ as a secondary oxidation product in the system. By analogy to the established oxidation mechanism of CH_3CHO[25] and C_2F_5CHO,[26] it seems likely that the source of $CF_3(CF_2)_3CH_2COOH$ is reaction of $CF_3(CF_2)_3CH_2C(O)OO\bullet$ radicals (formed in reactions 2−6) with HO_2 radicals

$$CF_3(CF_2)_3CH_2C(O)OO\bullet + HO_2 \rightarrow CF_3(CF_2)_3CH_2COOH + O_3 \quad (12a)$$

If reaction 12a is the source of $CF_3(CF_2)_3CH_2COOH$, then ozone should be observed and should have a product profile similar to that of $CF_3(CF_2)_3CH_2COOH$. Characteristic IR features of O_3 at 1000−1100 cm^{-1} were detected in the product spectra. Figure 5 shows a plot of the observed formation of ozone and $CF_3(CF_2)_3CH_2COOH$ versus loss of the aldehyde, $CF_3(CF_2)_3CH_2CHO$, normalized for the initial alcohol concentration. The initial yield of ozone is indistinguishable from that of $CF_3(CF_2)_3CH_2COOH$ suggesting that reaction 12a is the source of both $CF_3(CF_2)_3CH_2COOH$ and O_3. The ozone profile in Figure 5 is much more curved than that of $CF_3(CF_2)_3CH_2COOH$, reflecting the more reactive nature of Cl atoms toward ozone than $CF_3(CF_2)_3CH_2COOH$. The rate constant for reaction of Cl atoms with O_3, $k(Cl + O_3) = 1.2 \times 10^{-11}$, is comparable to that for the primary product, $k(Cl + CF_3(CF_2)_3CH_2CHO) = (1.84 \pm 0.30) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}. In contrast, by

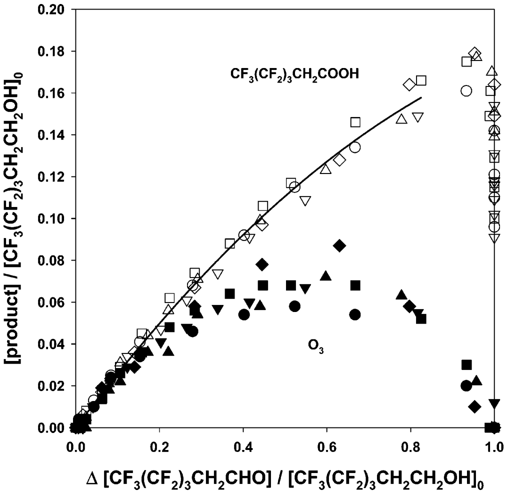

Figure 5. Formation of $CF_3(CF_2)_3CH_2COOH$ (open symbols) and ozone (filled symbols) versus the loss of $CF_3(CF_2)_3CH_2CHO$, normalized to the initial alcohol concentration. Experiments were performed in 700 Torr of N_2/O_2 diluent. Partial pressures of O_2 were 10 Torr, circles; 140 Torr, triangles up and down; 400 Torr, squares; and 700 Torr, diamonds.

analogy to the existing data for reaction of fluorinated carboxylic acids toward Cl atoms,[26] it is expected that the reactivity of Cl atoms toward the acid $CF_3(CF_2)_3CH_2COOH$ will be substantially less than toward the aldehyde $CF_3(CF_2)_3CH_2CHO$. The initial slope of the product profile of $CF_3(CF_2)_3CH_2COOH$ in Figure 4 gives a molar yield of 0.27 ± 0.01 for the formation of this species following Cl atom initiated oxidation of $CF_3(CF_2)_3CH_2CHO$.

3.5. Formation of $CF_3(CF_2)_3CH_2C(O)OOH$ as a Secondary Oxidation Product. Although we cannot positively identify the unknown shown in Figure 1E, there are several pieces of information that lead us to believe that the unknown is the peracid $CF_3(CF_2)_3CH_2C(O)OOH$. The evidence is (i) the IR features scale linearly in all experiments (suggesting they are associated with one compound), (ii) their formation follows the pattern expected from a secondary product (see Figure 4), (iii) the IR features have frequencies consistent with those expected from $CF_3(CF_2)_3CH_2C(O)OOH$, and (iv) given the observation of the acid $CF_3(CF_2)_3CH_2COOH$ and O_3 as products of reaction 14 it would be expected by analogy to the oxidation mechanism of CH_3CHO that the peracid will also be formed in the system.

As part of this study, a sample of $CF_3C(O)OOH$ was prepared and a calibrated IR spectrum of this species was recorded. The main IR features, together with the IR absorption cross sections (cm^2 molecule^{-1}), are 1148 cm^{-1} (2.01×10^{-18}), 1209 cm^{-1} (1.40×10^{-18}), 1237 cm^{-1} (1.75×10^{-18}), and 1808 cm^{-1} (6.0×10^{-19}). Figure 6 shows a comparison of the residual with the IR spectrum of $CF_3C(O)OOH$ at 1300−1900 and 3100−3600 cm^{-1}. The spectra have similar features at 890 cm^{-1} (O−O stretch), 1450 cm^{-1} (O−H bend), 1776 cm^{-1} (carbonyl stretch), and 3328 cm^{-1} (O−H stretch). The spectrum of the unknown is consistent with its assignment as the peracid, $CF_3(CF_2)_3CH_2C(O)OOH$.

The atmospheric oxidation of acetaldehyde, CH_3CHO, proceeds via the formation of acetyl peroxy radicals, $CH_3C(O)OO\bullet$. Acetyl peroxy radicals react with HO_2 via two channels.[27−31]

$$CH_3C(O)OO\bullet + HO_2 \rightarrow CH_3C(O)OOH + O_2 \quad (13a)$$

$$CH_3C(O)OO\bullet + HO_2 \rightarrow CH_3COOH + O_3 \quad (13b)$$

Tyndall et al.[25] recommend $k_{13b}/(k_{13a} + k_{13b}) = 0.20$ in one atmosphere of air at 298 K. It seems reasonable to believe that the reaction of $CF_3(CF_2)_3CH_2C(O)OO\bullet$ with HO_2 will proceed via two channels and that the peracid will be formed.

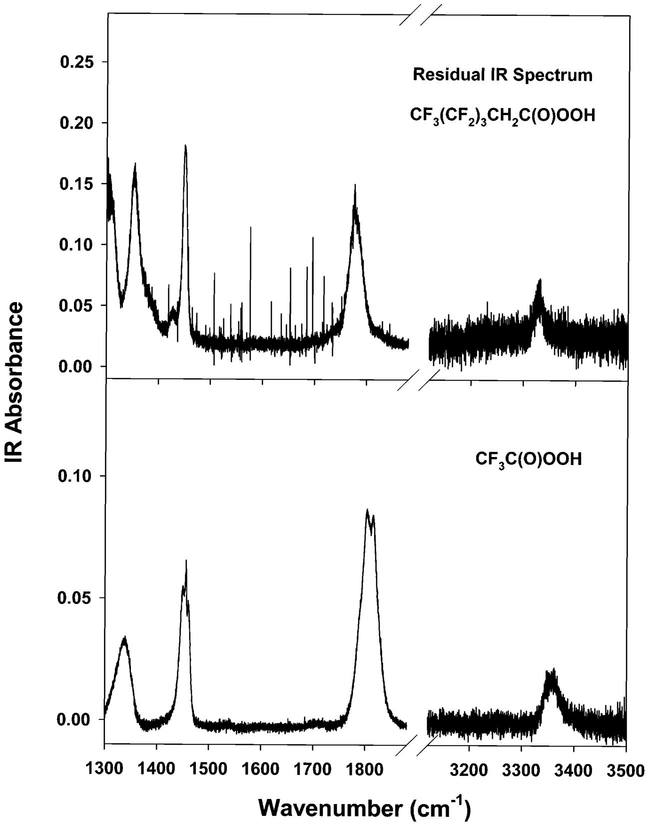

Figure 6. IR spectra of the unknown (top panel) and $CF_3C(O)OOH$ (bottom panel).

$$CF_3(CF_2)_3CH_2C(O)OO\bullet + HO_2 \rightarrow CF_3(CF_2)_3CH_2COOH + O_3 \quad (12a)$$

$$CF_3(CF_2)_3CH_2C(O)OO\bullet + HO_2 \rightarrow CF_3(CF_2)_3CH_2C(O)OOH + O_2 \quad (12b)$$

As seen in Figure 4, the concentration of the unknown increases proportionately with that of $CF_3(CF_2)_3CH_2COOH$ in a manner consistent with that expected if the unknown was the peracid $CF_3(CF_2)_3CH_2C(O)OOH$. In light of the discussion above, we conclude that the unknown is $CF_3(CF_2)_3CH_2C(O)OOH$. In the absence of a calibrated reference spectrum, it is not possible to quantify the peracid yield at the present time; however, since the yield of $CF_3(CF_2)_3CHO$ is 0.46 and the yield of $CF_3(CF_2)_3CH_2COOH$ is 0.27, carbon balance requires that the yield of $CF_3(CF_2)_3CH_2C(O)OOH$ is ≤ 0.27. The peracid yields given in Figure 4 are in arbitrary units.

3.6. Formation of the Products $CF_3(CF_2)_3COOH$, COF_2, and CF_3OH. As shown in Figure 4 for all experiments, when consumption of the parent alcohol and the aldehyde primary product is large (>90%), there is a significant decrease in the yield of the three secondary products. This behavior presumably reflects loss of the secondary products ($CF_3(CF_2)_3CHO$, $CF_3(CF_2)_3CH_2COOH$, and $CF_3(CF_2)_3CH_2C(O)OOH$) via reaction with Cl atoms. Concurrent with the loss of the secondary products, an increase in the concentrations of $CF_3(CF_2)_3COOH$, COF_2, and CF_3OH was observed. This behavior can be seen from a comparison of Figure 7 showing the formation of $CF_3(CF_2)_3COOH$, COF_2, and CF_3OH, with Figure 4 showing the loss of the secondary products. We conclude that

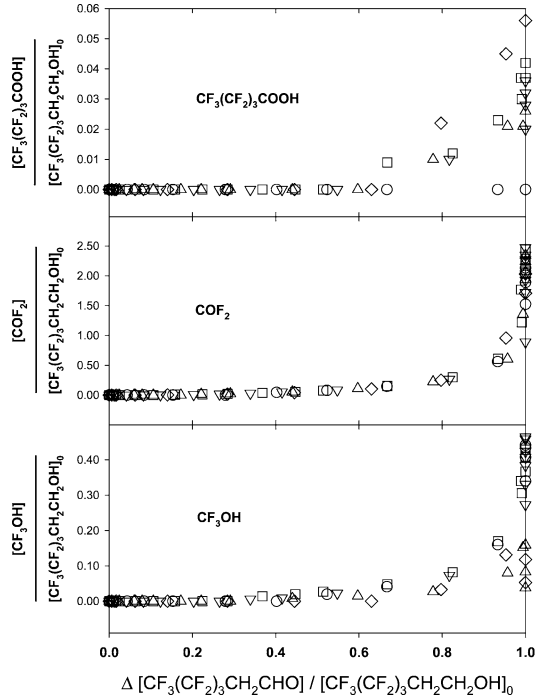

Figure 7. Formation of $CF_3(CF_2)_3COOH$, COF_2, and CF_3OH versus the loss of $CF_3(CF_2)_3CH_2CHO$, normalized for the initial alcohol concentration. Experiments were performed in 700 Torr of N_2/O_2 diluent. Partial pressures of O_2 were 10 Torr, circles; 140 Torr, triangles up and down; 400 Torr, squares; and 700 Torr, diamonds.

$CF_3(CF_2)_3COOH$, COF_2, and CF_3OH are tertiary products of 4:2 FTOH oxidation.

Analogous to the formation of $CF_3(CF_2)_3CH_2COOH$ from $CF_3(CF_2)_3CH_2CHO$ (see section 3.4), and C_2F_5COOH from C_2F_5CHO,[26] it seems likely that $CF_3(CF_2)_3COOH$ is formed during oxidation of $CF_3(CF_2)_3CHO$.

$$CF_3(CF_2)_3CHO + Cl \rightarrow CF_3(CF_2)_3C{\bullet}O + HCl \qquad (14)$$

$$CF_3(CF_2)_3C{\bullet}O + O_2 \rightarrow CF_3(CF_2)_3C(O)OO{\bullet} \qquad (15)$$

$$CF_3(CF_2)_3C(O)OO{\bullet} + HO_2 \rightarrow CF_3(CF_2)_3COOH + O_3 \qquad (16)$$

In the present experiments, irradiations were continued until the parent alcohol, $CF_3(CF_2)_3CH_2CH_2OH$, the primary product, $CF_3(CF_2)_3CH_2CHO$, and the secondary product, $CF_3(CF_2)_3CHO$, were consumed completely (>98%). Figure 8 shows spectra before (A) and after (B) 8.5 min of irradiation of a gas mixture consisting of 34.4 Torr $CF_3(CF_2)_3CH_2CH_2OH$ and 100 mTorr Cl_2 in 700 Torr air. During the irradiation, all of the parent alcohol, $CF_3(CF_2)_3CH_2CH_2OH$, all of the primary product, $CF_3(CF_2)_3CH_2CHO$, and all of the secondary product, $CF_3(CF_2)_3CHO$, were consumed. Panel C shows the product spectrum after the removal of features due to $CF_3(CF_2)_3CH_2COOH$, $CF_3(CF_2)_3CH_2C(O)OOH$, COF_2, and CF_3OH. Comparison of the residual spectrum with a reference spectrum of $CF_3(CF_2)_3COOH$ (D) clearly shows formation of the perfluorinated acid. Using such conditions, the molar yields of the perfluorinated acid from 4:2 FTOH was <0.011, 0.031, 0.042, and 0.056 for 10, 140, 400, and 700 Torr O_2, respectively. The increase in acid yield with the oxygen concentration implies that there are competing reactions involving O_2 in the system; however, the nature of these reactions is unknown at present.

Hurley et al.[22] have reported that the Cl initiated oxidation of $CF_3(CF_2)_nCH_2OH$ ($n = 0-3$) gives $CF_3(CF_2)_nCHO$ in a yield which is indistinguishable from 100% and that subsequent reaction of Cl with $CF_3(CF_2)_nCHO$ gives the acids, $CF_3(CF_2)_nCOOH$, in yields of 25% ($n = 0$), 18% ($n = 1$), 7% ($n = 2$), and 6% ($n = 3$). In the current study, $CF_3(CF_2)_3CHO$ is formed in a yield of 46% (see section 3.3). On the basis of the previous work of Hurley et al.,[22] the $CF_3(CF_2)_3COOH$ yield in the presence of 140 Torr oxygen is expected to be 0.47 × 0.06 = 0.03. The yield of $CF_3(CF_2)_3COOH$ observed in the present work is consistent with the previous work by Hurley et al.[22]

The observed COF_2 and CF_3OH are the products expected from decomposition of the $CF_3(CF_2)_3$ tail of $CF_3(CF_2)_3CH_2CH_2OH$ which "unzips" through the following reactions:

$$CF_3(CF_2)_2C{\bullet}F_2 + O_2 \rightarrow CF_3(CF_2)_2CF_2OO{\bullet} \qquad (17)$$

$$CF_3(CF_2)_2CF_2OO{\bullet} + ROO{\bullet} \rightarrow CF_3(CF_2)_2CF_2O{\bullet} + RO{\bullet} + O_2 \qquad (18)$$

$$CF_3(CF_2)_2CF_2O{\bullet} \rightarrow CF_3CF_2C{\bullet}F_2 + COF_2 \qquad (19)$$

$$CF_3CF_2C{\bullet}F_2 + O_2 \rightarrow CF_3CF_2CF_2OO{\bullet} \qquad (20)$$

$$CF_3CF_2CF_2OO{\bullet} + ROO{\bullet} \rightarrow CF_3CF_2CF_2O{\bullet} + RO{\bullet} + O_2 \qquad (21)$$

$$CF_3CF_2CF_2O{\bullet} \rightarrow CF_3C{\bullet}F_2 + COF_2 \qquad (22)$$

$$CF_3C{\bullet}F_2 + O_2 \rightarrow CF_3CF_2OO{\bullet} \qquad (23)$$

$$CF_3CF_2OO{\bullet} + ROO{\bullet} \rightarrow CF_3CF_2O{\bullet} + RO{\bullet} + O_2 \qquad (24)$$

$$CF_3CF_2O{\bullet} \rightarrow C{\bullet}F_3 + COF_2 \qquad (25)$$

$$C{\bullet}F_3 + O_2 \rightarrow CF_3OO{\bullet} \qquad (26)$$

$$CF_3OO{\bullet} + ROO{\bullet} \rightarrow CF_3O{\bullet} + RO{\bullet} + O_2 \qquad (27)$$

$$CF_3O{\bullet} + HO_2 \rightarrow CF_3OH + O_2 \qquad (28)$$

4. Implications for Atmospheric Chemistry. The goal of the present work was to provide insight into the atmospheric oxidation mechanism of fluorotelomer alcohols. The atmospheric oxidation of 4:2 FTOH is initiated by reaction with OH radicals. Cl atoms and OH radicals react with 4:2 FTOH via the same mechanism (abstraction of a hydrogen atom α to the OH group) and give the same radical products.[4] Hence, a study of the Cl atom initiated oxidation provides information concerning the OH radical initiated atmospheric degradation of 4:2 FTOH. Given the structural similarity of 4:2 FTOH to longer chain commercially important fluorotelomer alcohols (e.g., 6:2 FTOH, 8:2 FTOH, 10:2 FTOH), the atmospheric oxidation mechanism for 4:2 FTOH is likely to be similar to the longer chain fluorotelomer alcohols. Hence, products of the Cl atom initiated oxidation of 4:2 FTOH identified herein are likely to provide insight into the atmospheric degradation mechanism of FTOHs.

The present work provides a detailed description of the products and mechanism of the Cl atom initiated oxidation of 4:2 FTOH in the absence of NO_x. We show that $CF_3(CF_2)_3CH_2CHO$ is the primary atmospheric oxidation product of 4:2 FTOH. This result is consistent with the previous finding by LeBras et al.[5] that the yield of CF_3CH_2CHO from oxidation of $CF_3CH_2CH_2OH$ in the presence and absence of NO_x was in the range 50−100%. $CF_3(CF_2)_3CH_2CHO$ is formed via reaction of $CF_3(CF_2)_3CH_2C{\bullet}HOH$ radicals with O_2. Reaction with O_2 will dominate the atmospheric loss of $CF_3(CF_2)_3CH_2C{\bullet}HOH$ radicals. The presence of NO_x should have no impact on the $CF_3(CF_2)_3$-

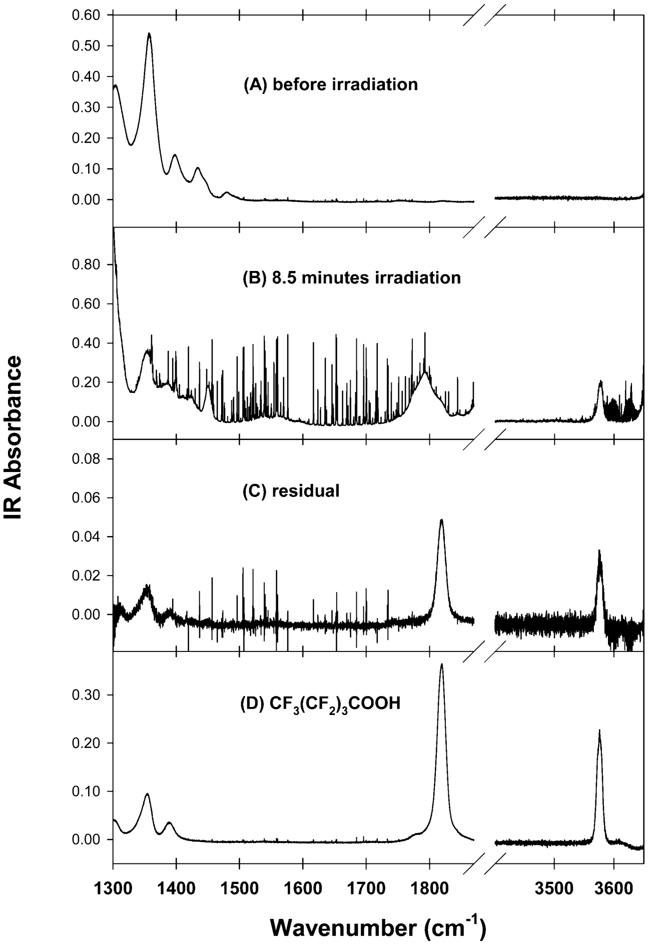

Figure 8. IR spectra obtained before (A) and after (B) 8.5 min of irradiation of a mixture of 34.4 mTorr $CF_3(CF_2)_3CH_2CH_2OH$ and 100 mTorr Cl_2 in 700 Torr air. Panel C shows the residual spectrum obtained by subtracting the IR features of $CF_3(CF_2)_3CH_2COOH$, $CF_3(CF_2)_3CH_2C(O)OOH$, COF_2, and CF_3OH from the spectrum shown in B. Panel D is the reference spectra of $CF_3(CF_2)_3COOH$.

CH_2CHO yield. We conclude that the atmospheric oxidation of FTOHs of the general formula $CF_3(CF_2)_nCH_2CH_2OH$ gives the aldehyde $CF_3(CF_2)_nCH_2CHO$ in a yield close to 100%.

Oxidation of the primary product $CF_3(CF_2)_3CH_2CHO$ in the absence of NO_x gives the secondary products $CF_3(CF_2)_3CHO$, $CF_3(CF_2)_3CH_2COOH$, and $CF_3(CF_2)_3CH_2C(O)OOH$. Plausible mechanisms for the formation of these species are provided in sections 3.3, 3.4, and 3.5. These compounds are likely to be formed during the atmospheric oxidation of FTOHs in low NO_x environments. The formation of $CF_3(CF_2)_nCH_2COOH$ and $CF_3(CF_2)_nCH_2C(O)OOH$ as FTOH oxidation products has not been reported previously. In areas with high NO_x concentrations (e.g., within and downwind of urban areas), it is unlikely that either $CF_3(CF_2)_nCH_2COOH$ or $CF_3(CF_2)_nCH_2C(O)OOH$ will be formed to any appreciable extent. The production of these species requires reaction of an acyl peroxy with a HO_2 radical and both of these species will be removed rapidly via reaction with NO_x. Formation of $CF_3(CF_2)_nCHO$ during FTOH oxidation will probably still be significant in the presence of NO_x because there are rapid reactions involving NO_x which will form this product (e.g., reactions 7−11 with NO, rather than RO_2, converting the peroxy radicals into alkoxy radicals). LeBras et al.[5] have reported the formation of CF_3CHO following the OH initiated oxidation of $CF_3CH_2CH_2OH$ in the presence of NO_x.

We identify $CF_3(CF_2)_3COOH$, COF_2, and CF_3OH as products of 4:2 FTOH oxidation. COF_2 and CF_3OH are formed during the "unzipping" of the $CF_3(CF_2)_3$ tail via reactions 17−28. COF_2 and, to a lesser extent, CF_3OH are also expected to be formed in the presence of NO_x. The formation of COF_2 and CF_3OH in the concentrations expected from atmospheric degradation of FTOHs is of no environmental concern and will not be discussed further.

In the present work, we identify $CF_3(CF_2)_3COOH$ as a product in a small, but discernible, yield from the Cl atom initiated oxidation of 4:2 FTOH in the absence of NO_x. Reaction 16 is the likely source of $CF_3(CF_2)_3COOH$. Reaction 16 is likely to occur in the atmosphere in low NO_x environments; hence, $CF_3(CF_2)_3COOH$ is expected to be formed as a product of the atmospheric degradation of 4:2 FTOH. Generalizing this result, it seems reasonable to conclude that perfluorinated acids, $CF_3(CF_2)_nCOOH$, will be formed during the atmospheric oxidation of other FTOHs in low NO_x environments. This is an important conclusion given the current interest in the environmental formation, fate, and impact of perfluorinated acids (see section 1). At this point, we stress that the present experiments were conducted in the absence of NO_x. The source of $CF_3(CF_2)_3COOH$ in the present experiments, reaction 16, will not be significant in environments with high NO_x. In such environments, reaction with NO_x (leading to the formation of COF_2 and $CF_3(CF_2)_3C(O)O_2NO_2$) will be the dominant loss mechanism for $CF_3(CF_2)_3C(O)O_2$ radicals.

Chemical activation effects which can be important in determining products following reaction of peroxy radicals with NO[32] will not play a role in determining the perfluorocarboxylic acid yield during the atmospheric oxidation of 4:2 FTOH for two reasons. First, the majority of alkoxy radicals formed during the oxidation (e.g., $CF_3(CF_2)_3CH_2C(O)O$, $CF_3(CF_2)_nO$) have only one fate: decomposition via C−C bond scission. Chemical activation would speed up, but not change, this process. Second, $CF_3(CF_2)_3CH_2O$ is the only alkoxy radical formed during the oxidation which could, in principle, exhibit a chemical activation effect. However, this radical would only show the effect (fragmentation into a $CF_3(CF_2)_3$ radical and HCHO) when NO_x was present in the system and this would only serve to preclude a process (reaction 16) which, as discussed above, will not be important in the presence of NO_x.

The present work serves to clarify the atmospheric oxidation mechanism of FTOHs. We have established qualitatively that FTOHs are a source of perfluorocarboxylic acids. However, the magnitude, and hence significance, of this source is unclear. Kinetic data for the competing atmospheric reactions of the radical species discussed herein and a regional, or hemispheric, modeling study are needed to quantify the contribution of FTOH degradation to the environmental perfluorocarboxylic acid burden.

Acknowledgment. M.P.S.A. thanks the Danish Research Agency for a research grant. This research was funded, in part, by an NSERC Strategic Grant.

References and Notes

(1) Telomer Research Program Update, Presentation to USEPA-OPPT, November 25, 2002; U.S. Public Docket AR226-1141.

(2) Martin, J. W.; Muir, D. C. G.; Moody, C. A.; Ellis, D. A.; Kwan, W. C.; Solomon, K. R.; Mabury, S. A. *Anal. Chem.* **2002**, *74*, 584.

(3) Stock, N. L.; Lau, F. K.; Ellis, D. A.; Martin, J. W.; Muir D. C. G.; Mabury, S. A. *Environ. Sci. Technol.* **2004**, *38*, 991.

(4) Ellis, D. A.; Martin, J. W.; Mabury, S. A.; Hurley, M. D.; Sulbaek Andersen, M. P.; Wallington, T. J. *Environ. Sci. Technol.* **2003**, *37*, 3816.

(5) Le Bras, G.; Bossoutrot, V.; Magneron, I. *Study of the Atmospheric Fate of Fluorinated Alcohols*; Final Report to the Fluorotelomer Research Program; July 2003.

(6) Ellis, D. A.; Moody, C. A.; Mabury, S. A. Part N Organofluorines. In *Handbook of Environmental Chemistry*; Nielson, A., Ed.; Springer-Verlag: Heidelberg, 2002; Chapter 3.

(7) Scott, B. F.; Spencer, C.; Moody, C. A.; Mabury, S. A.; MacTavish, D.; Muir, D. C. G. Poster presented at the 13th Annual SETAC Europe Meeting, Hamburg, DE, 2003.

(8) Martin, J. W.; Mabury, S. A.; Solomon, K. R.; Muir, D. C. G. *Environ. Toxicol. Chem.* **2003**, *22*, 196.

(9) Martin, J. W.; Smithwick, M. M.; Braune, B. M.; Hekstra, P. F.; Muir, D. C. G.; Mabury, S. A. *Environ. Sci. Technol* **2004**, *38*, 373.

(10) Berthiaume, J.; Wallace, K. B. *Toxicol. Lett.* **2002**, *129*, 23.

(11) Upham, B. L.; Deocampo, N. D.; Wurl, B.; Trosko, J. E. *Int. J. Cancer* **1998**, *78*, 491.

(12) Biegel, L. B.; Hurtt, M. E.; Frame, S. R.; Connor, J. O.; Cook, J. C. *Toxicol. Sci.* **2001**, *60*, 44.

(13) *Preliminary risk assessment of the developmental toxicity associated with exposure to perfluorooctanoic acid and its salts*; U.S. Environmental Protection Agency, Office of Pollution Prevention and Toxics, Risk Assessment Division, 2003.

(14) Frank, H.; Christoph, E. H.; Holm-Hansen, O.; Bullister, J. L. *Environ. Sci. Technol.* **2002**, *36*, 12.

(15) Ellis, D. A.; Mabury, S. A.; Martin, J. W.; Muir, D. C. G. *Nature* **2001**, *412*, 321.

(16) Hurley, M. D.; Sulbaek Andersen, M. P.; Wallington, T. J.; Ellis, D. A.; Martin, J. W.; Mabury, S. A. *J. Phys. Chem. A* **2004**, *108*, 615.

(17) Ellis, D. A.; Martin, J. W.; De Silva, A. O.; Mabury, S. A.; Hurley, M. D.; Sulbaek Andersen, M. P.; Wallington, T. J. *Environ. Sci. Technol.* **2004**, in press.

(18) Wallington, T. J.; Japar, S. M. *J. Atmos. Chem.* **1989**, *9*, 399.

(19) Achilefu, S.; Mansuy, L.; Selve, C.; Thiebaut, S. *J. Fluorine Chem.* **1995**, *70*, 19.

(20) Lévêque, L.; Le Blanc, M.; Pastor, R. *Tetrahedron Lett.* **1998**, *39*, 8857−8860.

(21) Kopitsky, R.; Willner, H.; Hermann, A.; Oberhammer, H. *Inorg. Chem.* **2001**, *40*, 2693.

(22) Hurley, M. D.; Wallington, T. J.; Sulbaek Anderson, M. P.; Ellis, D. A.; Martin, J. W.; Mabury, S. A. *J. Phys. Chem. A* **2004**, *108*, 1973.

(23) Meagher, R. J.; McIntosh, M. E.; Hurley, M. D.; Wallington, T. J. *Int. J. Chem. Kinet.* **1997**, *29*, 619.

(24) Sulbaek Andersen, M. P.; Nielsen, O. J.; Hurley, M. D.; Ball, J. C.; Wallington, T. J.; Stevens, J. E.; Martin, J. W.; Ellis, D. A.; Mabury, S. A. *J. Phys. Chem. A* **2004**, in press.

(25) Tyndall, G. S.; Cox, R. A.; Granier, C.; Lesclaux, R.; Moortgat, G. K.; Pilling, M. J.; Ravishankara, A. R.; Wallington, T. J. *J. Geophys. Res.* **2001**, *106*, 12157.

(26) Sulbaek Andersen, M. P.; Hurley, M. D.; Wallington, T. J.; Ball, J. C.; Martin, J. W.; Ellis, D. A.; Mabury, S. A.; Nielsen, O. J. *Chem. Phys. Lett.* **2003**, *381*, 14.

(27) Stockwell, W. R.; Milford, J. B.; Dongfen, G.; Yang, Y.-J. *J. Atmos. Environ.* **1995**, *29*, 1591.

(28) Niki, H.; Maker, P. D.; Savage, C. M.; Breitenbach, L. P. *J. Phys. Chem.* **1985**, *89*, 588.

(29) Moortgat, G. K.; Veyret, B.; Lesclaux, R. *Chem. Phys. Lett.* **1989**, *160*, 443.

(30) Horie, O.; Moortgat, G. K. *J. Chem. Soc., Faraday Trans.* **1992**, *88*, 3305.

(31) Crawford, M.; Wallington, T. J.; Szente, J. J.; Maricq, M. M.; Francisco, J. S. *J. Phys. Chem.* **1999**, *103*, 365.

(32) Wallington, T. J.; Hurley, M. D.; Fracheboud, J. M.; Orlando, J. J.; Tyndall, G. S.; Sehested, J.; Møgelberg, T. E.; Nielsen O. J. *J. Phys. Chem.* **1996**, *100*, 18116.